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<p>(54) Title: ULTRAVIOLET-CURABLE BLENDS OF VINYL ETHER POLYURETHANES AND UNSATURATED ELASTOMERS AND COATINGS CONTAINING THE SAME</p> <p>(57) Abstract</p> <p>Liquid mixtures which are curable on exposure to actinic radiation when catalyzed with a cationic photoinitiator comprise vinyl ether-terminated polyurethane and an ethylenically unsaturated liquid polymeric elastomer are disclosed. The unsaturated elastomer participates in the cationic cure and softens the cured coatings. For this purpose the elastomer is present in an amount of from 0.1 % to 40 % based on the total weight of the mixture thereof with the polyurethane.</p>			

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ULTRAVIOLET-CURABLE BLENDS OF VINYL ETHER  
POLYURETHANES AND UNSATURATED ELASTOMERS  
AND COATINGS CONTAINING THE SAME

DESCRIPTION

5      Technical Field

This invention relates to ultraviolet-curable blends of vinyl ether-terminated polyurethanes and ethylenically unsaturated elastomers, and includes coatings containing these blends. These blends include a catalyst which initiates a cationic cure when exposed to actinic radiation, the unsaturated elastomer participating in the cure and functioning to soften the cured coatings.

10     Background Art

15     Ultraviolet-curable coatings based on acrylate-terminated polyurethanes are well known. Many of the rapidly curing polyurethanes carrying terminal acrylate groups are too hard for some purposes, such as primer coatings for optical glass fiber, so these are combined with liquid materials which function to soften the films which are produced on cure. Ethylenically unsaturated elastomers have been tried as softening agents since some of these are long chain molecules which might soften the cured coatings.

20     Unfortunately, these unsaturated elastomers have not been useful because the ethylenic unsaturation contained within these elastomers does not satisfactorily participate in the free-radical initiated cure, leaving ethylenic unsaturation in the cured product. This residual ethylenic unsaturation remains reactive so that the cured films age, probably by reaction with atmospheric oxygen, to harden the cured films with time. This hardening leads to embrittlement, especially at low temperature.

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As a result of this adverse experience with ethylenically unsaturated elastomers in acrylate-terminated radiation-curable mixtures, such mixtures were not regarded as appropriate materials to soften ultraviolet-curable compositions.

5       Summary of the Invention

The present invention provides liquid mixtures (blends) of vinyl ether-terminated polyurethanes and ethylenically unsaturated liquid polymeric elastomers 10 which are substantially free of hydroxy functionality and which are curable with actinic light in or near the ultraviolet range in the presence of a cationic photoinitiator. The invention includes coating compositions containing these blends in admixture with an 15 amount of a cationic photoinitiator which is effective to initiate a cationic cure when exposed to actinic light. It is surprising to find that the unsaturated elastomer participates in the cationic cure even though it does not participate in a conventional free-radical polymerization. 20 In the coatings of this invention, the unsaturated elastomer functions to soften the cured coatings.

It is desired to stress that polyvinyl ethers of polyols are useful diluents for vinyl ether-terminated polyurethanes, and can be regarded as polyfunctional reactive diluents. But these polyfunctional reactive 25 diluents generally function to harden the cured composition. Monovinyl ethers are usually somewhat volatile, and hence it is preferred not to employ them in ultraviolet-curable coatings which are desirably free of volatile components. This leaves little opportunity to 30 enhance the softness of the cured coatings, so it is desired to minimize the proportion of such reactive diluents herein, or at least to minimize their hardening action by introducing a softening action to counterbalance 35 it.

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Despite these difficulties it is desirable to be able to use vinyl ether-terminated polyurethanes for the production of softer coatings because the vinyl ethers are less toxic and less troublesome than the corresponding acrylate-terminated materials, and also because the cationic cure is very rapid in some instances. These coatings are especially adapted for the coating of optical glass fibers in which the increased softness contributed by the unsaturated elastomer is needed to allow the coatings to contact the glass surface of such fibers without introducing low temperature microbending difficulties.

The vinyl ether-terminated polyurethanes are themselves known, and these tend to be hard and brittle when cured, albeit those of relatively lower molecular weight are harder and more brittle than those of relatively higher molecular weight. Regardless of the hardness of the cured polyurethane, for some purposes it is desired to soften these. Softness is here measured by a reduced tensile strength and a reduced modulus of elasticity. It is found that from about 0.1% to about 40%, preferably from 0.5% to 20%, of the ethylenically unsaturated liquid polymeric elastomer based on the total weight of the elastomer and polyurethane, serves to provide desired softness when the mixture is cured by a cationic cure. This action is of special importance when the polyurethane is of higher molecular weight since these polyurethanes are of higher viscosity and require more reactive diluent to provide coating viscosity. The liquid unsaturated polymeric elastomers used herein not only add softness, but they can decrease the proportion of reactive diluent needed to apply the compositions.

It is stressed that saturated elastomers are not useful herein. This is because saturated elastomers retard the cure and render it sluggish. The greater the

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proportion of saturated elastomer, the more it disturbs the desired cationic cure.

5 In contrast, the ethylenically unsaturated elastomers participate in the cationic cure, residual unsaturation is largely eliminated by that cure, and no difficulty has been encountered when the cured films were subjected to heat aging tests.

Detailed Description of the Invention

10 As previously indicated, the coating compositions of the present invention comprise a blend of a vinyl ether-terminated polyurethane and an ethylenically unsaturated liquid polymeric elastomer.

15 Vinyl ether-terminated polyurethanes are well known. These are made in conventional fashion from aliphatic monohydric vinyl ethers, which are known and available compounds. These monohydric vinyl ethers are formed in various ways, for example by reaction of a polyhydric alcohol, usually a diol, with acetylene in the presence of potassium hydroxide as catalyst. Thus, any 20 liquid diol, such as 1,4-butane diol, can be partially reacted to form the monovinyl ether, and this monovinyl ether can be separated and is available as such. Other aliphatic monohydric vinyl ethers can be made in the same or other ways. These monohydric vinyl ethers can be used 25 as an unsaturated capping agent for isocyanate-terminated oligomers in the same way that monohydric acrylates are used as capping agents to provide vinyl ether-terminated polyurethanes.

30 This invention will be illustrated using as the vinyl ether, the monovinyl ether of 1,4-butane diol, but it will be understood that other aliphatic monohydric vinyl ethers can be substituted therefor. These other vinyl ethers will be illustrated by the monovinyl ether of 1,4-cyclohexane dimethanol, 1,6-hexane diol, ethylene glycol, or triethylene glycol. Polyols of higher

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functionality used to provide a monohydric vinyl ether are illustrated by the divinyl ether of trimethylol propane or glycerin.

More particularly, the vinyl ether-terminated polyurethane is the reaction product of an aliphatic monohydric vinyl ether and an isocyanate-terminated oligomer which is the reaction product of an organic diisocyanate with a stoichiometric deficiency of material having a plurality of isocyanate-reactive hydrogen atoms, usually two. Vinyl ether-terminated polyurethanes are described in Bishop, Pasternack and Cutler U.S. Pat. No. 4,472,019 and also in Lapin and House patent 4,751,273. In each of these prior disclosures the vinyl ether-terminated polyurethane is formed by the reaction of an aliphatic monohydric vinyl ether with a diisocyanate. Many organic diisocyanates are disclosed in the Lapin and House disclosure, including those which are preferred herein.

The materials having a plurality of isocyanate-reactive hydrogen atoms are usually polyols or polyamines, and their use in stoichiometric deficiency forms isocyanate-terminated oligomers. The polyols are preferably diols, especially polyether diols, such as polyoxyethylene glycol, polyoxypropylene glycol or polytetrahydrofuran, but polyester diols, such as reaction products of diols with caprolactone, are also useful. These diols can have molecular weights of from about 60 to about 3,000, preferably from 300 to 2,000. The corresponding diamines are also useful, forming isocyanate-terminated polyureas instead of polyurethanes. Materials of higher functionality are illustrated by trimethylol propane and adducts thereof with alkylene oxides, such as propylene oxide. The terminal hydroxy groups in these polyols can be replaced by amine groups,

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preferably primary amine groups, to form polyamines which can be used herein.

These isocyanate-terminated oligomers are capped in this invention by reaction with an aliphatic monohydric vinyl ether which can be a monovinyl ether or a polyvinyl ether. After capping with the monohydric vinyl ether, the above-described isocyanate-terminated polyurethanes or polyureas all become vinyl ether-terminated polyurethanes and are referred to herein as polyurethanes.

It should be noted that capped polyurethanes can be made in many ways, as by forming an isocyanate-terminated oligomer followed by capping, by prereacting the capping agent with diisocyanate to form a monoisocyanate which is later reacted with polyol or polyamine, or by reacting all of the reactants together at the same time. All of these variations are acceptable and embraced by reference to the reaction product of an aliphatic monohydric vinyl ether, isocyanate-reactive polyol or polyamine, and sufficient organic polyisocyanate (preferably diisocyanate) to react with substantially all of the isocyanate-reactive functionality.

The urethane and urea-forming reactions are well known, being easily carried out by heating to moderate temperature, preferably in the presence of an appropriate catalyst, such as dibutyltin dilaurate. The reaction is usually forced by maintaining a temperature of from 40 C to 80 C to insure its completeness. The examples will adequately illustrate the urethane reaction, and reaction with urea can be carried out in the same way except to note that catalyst is not needed.

It is also preferred to employ certain aromatic diisocyanates, namely those which are alkylene bisphenyl diisocyanates. These are themselves well known. The alkylene group can contain from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms. These are

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illustrated by 1,2-diphenylethane diisocyanate and 1,3-diphenylpropane diisocyanate. It is preferred to employ compounds in which the two phenyl groups are carried by the same carbon atom so that the diisocyanate can be  
5 regarded as a derivative of methane. The preferred diisocyanate is 4,4'-diphenylmethane diisocyanate.

This invention is especially concerned with coatings which cure to possess sufficient softness for use in contact with the glass surface of optical glass fibers. For this purpose it is desired to employ vinyl ether-terminated polyurethanes having a number average molecular weight in the range of from about 1,500 to about 10 6,000. In the absence of the elastomer component, the lower end of this range was too hard for use in contact 15 with the optical glass surface, and the upper end of this range was too hard for use as a primary coating on optical glass fiber. The entire range of molecular weight is rendered softer by this invention, and hence is rendered more useful wherever increased softness is desired.  
20

The ethylenically unsaturated liquid polymeric elastomers are themselves well known and are hydrocarbons or halogen-substituted hydrocarbons. Liquid polymers of any diethylenically unsaturated C<sub>4</sub> or C<sub>5</sub> hydrocarbon or halogen-substituted hydrocarbon are appropriate, such as  
25 butadiene or chloroprene. These polymers are usually of oily liquid character, and those of low viscosity are preferred herein since these reduce the viscosity of the vinyl ether-terminated polyurethane which may be of excessive viscosity (higher than desired for coating  
30 application) or even of solid character. Polyisoprene will further illustrate the useful ethylenically unsaturated elastomers, and a liquid polyisoprene is presently preferred and will be used as illustrative.

The actinic light contemplated herein is  
35 desirably ultraviolet light, typically from 200 to 400

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nanometers, but the light wavelengths which can be used are intended to include visible light near the ultraviolet range as well as those within it. Thus, the word "actinic" light is used herein to include light having sufficient energy to initiate the cationic polymerization.

These coating compositions are catalyzed with a cationic photoinitiator which initiates a cationic cure when exposed to actinic light, usually a sulfonium compound. The proportion of said photoinitiator is an effective amount, preferably less than about 1.5% based on the weight of the unsaturated material present. The preferred proportion of catalyst is from 0.1% to 1.4%, most preferably from 0.2-1.0%, on the same weight basis.

The cationic photoinitiators are themselves well known and available in commerce. They are typically illustrated by sulfonium compounds, but iodonium compounds are also known cationic photoinitiators, as are diazo compounds. These compounds are used in the proportions which have already been discussed. A preferred, exemplary, catalyst is the triphenylsulfonium salt of hexafluorophosphate which is available in commerce from General Electric Co. under the trade designation UVE 1016. The commercial photoinitiator is supplied as a 50% solution in propylene carbonate. The tiny amount of this volatile solvent introduced with the catalyst is too small to disturb the essentially solvent-free character of the compositions used herein. On the other hand, the commercial catalyst compositions used in the examples herein are only 50% active (50% of the catalyst composition is constituted by propylene carbonate solvent), so only half of the commercial catalyst provides actual catalytic material.

The class of cationic photoinitiators is more fully discussed in U. S. Pat. No. 4,156,035 the disclosure of which is incorporated by reference. This patent

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indicated that any radiation sensitive aromatic onium salt of a group VIA element capable of releasing a Lewis acid when exposed to radiant energy can be used, triphenyl sulfonium fluoroborate, triphenyl sulfonium hexafluorophosphate and triphenyl sulfonium hexafluoroantimonate being particularly illustrated. This patent used these onium salts in combination with what it describes as carbonyl type photoinitiators, i.e. the aldehyde and ketone carbonyl compounds having at least one aromatic nucleus attached directly to the carbonyl group.

While such carbonyl type photoinitiators can also be present herein, it is presently preferred to use onium salts which are capable of functioning by themselves. Diaryliodonium salts, such as the 3M product sold under the trade name FC 509, are also contemplated, but these are normally used in combination with an aryl ketone photoinitiator, like benzophenone. The onium salts under consideration are also discussed in U.S. Pat. Nos. 4,069,055, 4,069,056 and 4,423,136.

Since iodonium salts normally require aryl ketones to also be present, it is preferred to employ triaryl sulfonium salts, such as the 3M product sold under the trade name FC 508 and the General Electric Co. products sold under the trade names UVE 1014 and UVE 1016. These sulfonium salts do not require aryl ketones to also be present.

The cationic cure is itself well known. Amines and carboxyl-functional compounds are known to be deleterious and hence there is no purpose in including them in the coating formulation. It was not known that small amounts of hydroxy functionality would inhibit the cure of vinyl ether systems. It has now been found that the addition of 0.1% of hydroxy functionality by weight of the composition causes the cationic cure in this invention to be about 3 times slower than if that hydroxy

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functionality had not been added. This will illustrate the importance of having a composition which is substantially hydroxy-free.

Thickness is important in this invention, the 5 cured coatings desirably having a thickness of from 1 to 10 mils, preferably from 2.5 to 6 mils. In the typical coating of optical glass fiber as contemplated herein, the coating applied to the glass has a thickness of about 3.0 mils, and it must be cured rapidly throughout that 10 thickness to provide a clear coating of only pale coloration having good physical properties including the capacity to resist considerable elongation without breaking and to resist water (both absorption and extraction).

15 The rapid cure of these relatively thick coatings is accomplished herein by the application of ultraviolet light in a dosage of at least about 0.5 J/sq cm., and usually somewhat more than that. The coatings evaluated herein have a thickness of about 3 mils and are 20 cured with an exposure of 0.75 J/sq cm in a first instance and with an exposure of 0.5 J/sq cm in a second instance.

It is desired to stress the significance of the proportion of cationic photoinitiator used in this 25 invention. When one uses the conventional proportion of 3% to 4% of the cationic photoinitiator with the vinyl ether-terminated polyurethanes of this invention, extreme discoloration of the cured film is encountered, and the cure is inhibited in that it does not extend completely through the film. Using 0.5 to 0.9% sulfonium 30 photoinitiator, as is here preferred, excellent cure speed is obtained, namely: a full cure extending completely through the film on an exposure of only 0.5 to 0.7 Joules/sq. cm. and the cured coatings are clear and of pale coloration, as previously indicated. Using acrylate- 35 terminated polyurethane compositions it is found that most

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of these require far more than 0.5 Joules/sq. cm. using a free radical photoinitiator, so the cures provided herein are at least about as rapid as those obtained with the conventional acrylate-functional compositions.

5 While the vinyl ether-terminated polyurethanes, the unsaturated elastomers and the photoinitiator can be the only materials present, other ethylenically unsaturated materials can also be present, especially vinyl ethers, like isobutyl vinyl ether, octyl vinyl ether, or polyvinyl ethers illustrated by the divinyl ether of 1,4-butane diol, 1,4-cyclohexane diol, or 1,6-hexane diol. These materials are reactive diluents, and they modify the reactivity and viscosity of the liquid coating compositions as well as the hardness of the cured product. It is stressed that while the polyvinyl ethers may introduce some hardness as they thin the coating composition, the elastomer component reduces this hardness.

20 Reactive diluents are not essential in this invention. When a reactive diluent is used, the vinyl ether-terminated polyurethanes desirably constitute from about 20% to 99% of the mixture with the reactive diluent, preferably from 30% to 80%. The elastomer component used herein is not regarded to be a reactive diluent herein, though some would place it in that category because it is reactive and liquid. The preferred reactive diluents are polyvinyl ethers of polyhydric compounds. These diluents lower viscosity while imparting only limited additional hardness to the composition.

25 30 As previously stressed, the urethane-forming reaction is pushed to completion to consume substantially all of the hydroxy functionality which is present. The substantial absence of hydroxy functionality is here defined to constitute a hydroxy content of less than 0.1% of the weight of the composition. Also, hydroxy-

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functional vinyl ethers are substantially absent from the composition when vinyl ethers which are not polyurethanes are used as reactive diluents. Thus, hydroxybutyl vinyl ether cannot be used as a diluent in this invention  
5 because this would increase the hydroxy content of the composition above the stated limit. Even small amounts of hydroxy functionality in the composition to be cured inhibits the cure, so the fastest curing compositions are those which contain the least hydroxy functionality.

10 It is preferred to cure the coatings of this invention in an atmosphere having a relatively low relative humidity, e.g., less than about 45%. The preferred range is less than 30%, and is usually at least about 15% because lower relative humidities are difficult  
15 to provide. We prefer to operate at 25% relative humidity, and all the results obtained herein were obtained with the films being cured in an atmosphere having a relative humidity of 25%.

20 These coatings are especially adapted to provide coatings for optical glass fibers in which a more rapid cure and increased softness in comparison with those obtainable from typical vinyl ether-terminated polyurethanes is needed to enable or enhance such utility. Primary coatings and single coating for optical glass  
25 fiber as well as ribbon coatings to assemble coated optical fiber in a ribbon provide preferred aspects of this invention. Actinically-cured coatings of general utility are also contemplated herein, this invention being useful whenever greater softness is desired.

30 Other advantages and features of this invention will become apparent to one skilled in the art from the examples tabulated below in which all parts are by weight.

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TABLE I

<u>Component</u>	<u>4017-162-A</u>	<u>Control (161C)</u>
------------------	-------------------	-----------------------

Vinyl ether-terminated

5	Polyurethane oligomer*	87.9	98.5
	Isolene 40**	9.8	----
	UVE 1016 (50% active)***	1.8	1.5
	DC 57!	0.25	----
	DC 190!	0.25	----

10

\* Silicone flow control agents from Dow-Corning.

15 \* A vinyl ether-terminated polyurethane oligomer prepared from 3 moles of triethylene glycol monovinyl ether, 3 moles of 4,4'-diphenylmethane diisocyanate and 1 mole of trimethylol propane in 50% solution in triethylene glycol divinyl ether.

20 \*\* A liquid cis-1,4 polyisoprene rubber of weight average molecular weight of 40,000 supplied by Hardman Incorporated of Bellesville, NJ (viscosity in the range of 36,000 to 55,000 cps. at 100 F).

25 \*\*\* UVE 1016 is G.E.'s cationic photoinitiator (triphenylsulfonium salt of hexafluorophosphate 50% solution in propylene carbonate).

All of the films were provided by drawdowns on  
 30 glass to provide a nominal thickness of 3 mils. The wet films were exposed to one D lamp and one H lamp to provide a dosage of 0.75 J/sq cm. The cured films were both light yellow in color, but the 161C film was clear while the 162 film was cloudy. The H & D lamps are similar in that each is 12 inches long and emits about 300 Watt per inch of length. The D lamp emission contains a greater proportion of longer waves which better penetrate the film and is preferred for the cure of thicker films. More particularly, the D lamp emits 25.6 Watt/inch at 200 to 35 300 nanometers, 63.8 Watt/inch at 300-400 nanometers and

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26.9 Watt/inch at 400-470 nanometers. The H lamp emits 44.8 Watt/inch at 200 to 300 nanometers, 31.0 Watt/inch at 300-400 nanometers and 17.7 Watt/inch at 400-470 nanometers.

5

TABLE IIProperties4017-162-AControl (161C)

	Water absorption*	12.3	8.9
	Extractables (%)*	4.2	3.1
10	Tensile, MPa	24	35
	% Elongation	5	7
	Modulus, MPa	650	925
	E' (100C MPa, 100 Mpa) °C	48, 66	52, 67
	Tan delta, max. °C	66	67
15	DMA Curve	unimodal	unimodal

\* indicates the results of tests in which the free coatings are immersed in water at 25 C for 24 hours.  
MPa identifies mega Pascals.

20

E', tan delta and DMA curve are the results of dynamic mechanical analysis. This is a known method for measuring mechanical stiffness and energy dissipation by imposing an oscillatory strain on the material and determining the resulting strain. E' is the elastic modulus. Tan delta is a ratio of the viscous modulus to the elastic modulus, and the DMA curves are obtained by plotting the various factors. When the plot shows more than one maximum, this indicates phase separation. The unimodal plot reported here indicates the material under test is a single continuous phase.

25

The data demonstrates that blending polyisoprene with the vinyl ether polyurethane oligomer results in significant reduction of the modulus and tensile strength without affecting the glass transition temperature. The percent elongation test requires many repetitions for

35

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accuracy and the results reported here are not regarded as determinative since only a single test result is reported. No significant changes in the dynamic mechanical properties are seen between 0 C and 100 C, and  
5 this retention of properties with change in temperature helps the composition to retain strength at elevated temperature.

10 The water sensitivity of both the blend and the control are high. This is due to the nature of the oligomer/diluent mixture which contains a high percentage of ether linkages.

15 The apparent increase in water sensitivity of the vinyl ether-terminated polyurethane-rubber blend is contrary to the expected behavior since polyisoprene is more hydrophobic than the polyether urethane backbone. This test's sensitivity to sample thickness may be responsible for the observed anomaly, so the reported results are not viewed as determinative unless the test  
20 is repeated many times to insure accuracy, and this was not done.

25 Although infrared analysis to determine the fate of the polyisoprene unsaturation during the cure was inconclusive, there is strong evidence that the liquid polyisoprene has in fact co-cured with the vinyl ether-terminated polyurethane as shown by the following experiment:

30 A cured film of 4017-162A, was refluxed in methyl ethyl ketone (MEK) for 8 hours followed by soaking in MEK for 72 hours. The film was then dried in a vacuum desiccator for 2 hours and then in air for 24 hours before reweighing. No weight change was observed after the described MEK extraction, and this is concluded to indicate the complete coreaction of the elastomer and the vinyl ether-terminated polyurethane during the cure.

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The effect of polyisoprene on the thermal stability of the blend was studied by heat aging a film of the blended material and the control at 200 C. The results appear below:

5

TABLE III  
Heat Aging at 200 Degrees C

10	Time (in hours)	Weight Loss			
		Sample (9.8% polyisoprene)		Control	
		%#	S.D.	%#	S.D.
	8	21.4	0.95	20.4	2.70
	32	32.5	1.73	30.3	3.53
	64	35.4	3.64	38.2	1.93
15	128	43.0	2.65	39.9	3.76
	200	45.6	2.89	44.7	3.42

# represents weight loss in percent following the noted exposure to temperature.

20 S.D. denotes standard deviation

Statistical analysis using t-distribution test statistic shows, with greater than 95% confidence, that the two materials possess the same thermal aging characteristics. This test compares the standard deviation obtained for the two samples to see whether they came from the same population, i.e., whether the mean values are the same with the specified level of confidence desired (here 95%).

Substituting a saturated thermoplastic rubber, 30 namely: a thermoplastic rubbery copolymer of poly(ethylene-butylene)-styrene, for the unsaturated elastomer used in the Table, inhibited the cure of the blend completely, and the stated radiation dosage produced no detectable cure.

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Additional tests were carried out to provide coatings having utility as primary coatings and single coatings for optical glass fiber. These tests were carried out by adding 5 and 10 parts of polyisoprene to a control which cured to provide a stronger and harder coating than desired. The addition of the polyisoprene did not noticeably vary the viscosity of the coatings, but it did require a somewhat larger amount of catalyst. The results are tabulated below.

10

TABLE IV

<u>Component</u>	<u>5% addition</u>	<u>10% addition</u>	<u>Control</u>
Oligomer sol'n*	67.4	63.8	72.0
TEGDVE	25.7	24.3	27.5
15 Isolene 40	4.9	9.9	---
DC 57	1.0	1.0	---
UVE 1016	1.0	1.0	0.5
<u>PROPERTIES</u>			
Dosage J/sq cm	0.5	0.5	0.5
20 Elongation, %	33	31	38
Tensile strength, MPa	2.7	2.7	12
Modulus, MPa	14	13	60

25 \* The oligomer solution used above was made with apparatus consisting of a 500 ml 4-necked round bottom flask fitted with a stirrer, dry nitrogen sparge, 250 ml addition funnel, reflux condenser, thermometer, and a thermostatically controlled heating mantle. 20.91 parts  
 30 of 4,4'-diphenylmethane diisocyanate were charged to the flask, and heated to 60 C. 22.74 parts of 1,4-butanediol divinyl ether were then added to the flask as a diluent and 7.45 parts of 4-hydroxybutyl vinyl ether were charged to the addition funnel and added over a 10 minute period.  
 35 The reaction mixture was held at 60 C for an additional

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two hours. The NCO content was then analyzed and the appropriate amount (to react with the unreacted isocyanate) of an adduct of caprolactone with diethylene glycol having a number average molecular weight of about 5 1,000 (Tone 220 supplied by Union Carbide Corporation, Chicago, IL can be used) was charged to the addition funnel. 0.06 part of dibutyltin dilaurate catalyst was then added to the flask and the addition funnel contents were added over a ten minute period while holding at 60 C. 10 Thereafter the flask was heated to 70 C and held at that temperature until the NCO content is less than 0.1%. By calculation, the number average molecular weight was determined to be 2400. TEGDVE is triethylene glycol divinyl ether.

15 As can be seen, the tensile strength and modulus are greatly reduced, the addition of 10% of polyisoprene not causing much more of a reduction than the addition of 5%, leading to the conclusion that a lesser modification can be obtained using a relatively small addition. Either 20 of the two additions makes the tested composition useful for either primary coating or single coating utility in the coating of optical glass fiber by applying a coating having a thickness of 3 mils to the freshly drawn fiber and then curing it with ultraviolet light as described 25 previously.

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WHAT IS CLAIMED IS:

1. A liquid mixture which is substantially free of hydroxy functionality and which is curable on exposure to actinic <sup>light</sup> when catalyzed with a cationic photoinitiator comprising, vinyl ether-terminated polyurethane and an ethylenically unsaturated liquid polymeric elastomer, said elastomer being present in an amount of from 0.1% to 40% based on the total weight of the mixture thereof with said polyurethane.
2. A mixture as recited in claim 1 in which said mixture includes a cationic photoinitiator in an amount effective to initiate cure, less than 1.5% based on the weight of the unsaturated material present.
3. A mixture as recited in claim 2 in which said photoinitiator is a sulfonium compound.
4. A mixture as recited in claim 3 in which said photoinitiator is present in an amount of from 0.1% to 1.4%.
5. A mixture as recited in claim 2 in which said photoinitiator is present in an amount of from 0.2% to 1.0%.
6. A mixture as recited in claim 1 in which said vinyl ether-terminated polyurethane is the reaction product of an aliphatic monohydric vinyl ether, isocyanate-reactive polyol or polyamine, and sufficient organic polyisocyanate to react with all of the isocyanate-reactive functionality.
7. A mixture as recited in claim 6 in which said polyisocyanate is a diisocyanate, and said isocyanate-reactive material is selected from diols and diamines having <sup>number average</sup> a molecular weight of from about 60 to about 3,000.
8. A mixture as recited in claim 7 in which

said diisocyanate is an alkylene bisphenyl <sup>material</sup> diisocyanate, and said isocyanate-reactive ~~polyol~~ is a diol having a molecular weight of from 300 to 2,000 to provide a vinyl ether-terminated polyurethane 5 having a molecular weight in the range of about 1,500 to about 6,000.

9. A mixture as recited in claim 1 in which a polyvinyl ether of a polyol is present as a reactive diluent.

10 10. A mixture as recited in claim 9 in which said vinyl ether-terminated polyurethane constitutes from about 20% to 99% of the mixture with said reactive diluent.

11. A mixture as recited in claim 9 in 15 which said vinyl ether-terminated polyurethane constitutes from 30% to 80% of the mixture with said reactive diluent.

12. A mixture as recited in claim 1 in which said elastomer is a liquid hydrocarbon polymer 20 or a liquid halogen-substituted hydrocarbon polymer.

12. A mixture as recited in claim 1 in which said elastomer is a liquid polymer of a diethylenically unsaturated hydrocarbon or a liquid polymer of a halogen-substituted hydrocarbon 25 containing 4 or 5 carbon atoms.

13. A mixture as recited in claim 1 in which said elastomer is polyisoprene.

14. A mixture as recited in claim 1 in which said composition contains less than 0.1% by 30 weight of the hydroxy group.

15. A substantially hydroxy-free coating composition which is curable on exposure to actinic radiation which comprises, a cationic photoinitiator, vinyl ether-terminated polyurethane which is the 35 reaction product of an aliphatic monohydric vinyl

ether, isocyanate-reactive polyol or polyamine, and sufficient organic diisocyanate to react with all of the isocyanate-reactive functionality, and an ethylenically unsaturated liquid polymeric elastomer  
5 which is a polymer of a diethylenically unsaturated hydrocarbon or a halogen-substituted hydrocarbon containing 4 or 5 carbon atoms., said elastomer being present in an amount of from 0.1% to 40% based on the total weight of the mixture thereof with said  
10 polyurethane.

16. A coating composition as recited in claim 15 in which said cationic photoinitiator is a sulfonium compound present in an amount of from 0.1% to ~~1.4%~~<sup>0.8%</sup> of the weight of the unsaturated material  
15 present.

17. A coating composition as recited in claim 15 in which said diisocyanate is 4,4'-diphenylmethane diisocyanate.

18. A method of coating a substrate  
20 comprising applying a film having a thickness of from 1 to 10 mils, of a substantially hydroxy-free, liquid, ultraviolet-curable composition comprising, a liquid mixture of a vinyl ether-terminated polyurethane, an ethylenically unsaturated elastomer,  
25 said elastomer being present in an amount of from 0.1% to 40% based on the total weight of the mixture thereof with said polyurethane, and an amount of a cationic photoinitiator which is effective to initiate a cationic cure when exposed to ultraviolet  
30 light, but less than 1.5% thereof based on the weight of the unsaturated material present, and exposing said film to ultraviolet light to cure the same.

19. A method as recited in claim 18 in which said film is exposed to light in an atmosphere  
35 having a relative humidity less than about 45%.

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20. A method as recited in claim 1 in which said polyurethane has a number average molecular weight in the range of from about 1,500 to about 6,000, and said film has a thickness of from 2.5 to 6  
5 mils.

21. An optical glass fiber coated with a cured coating of the composition of claim 1, said coating being in contact with the glass surface of said fiber.

10 22. A coated optical glass fiber as recited in claim 21 in which said polyurethane has a number average molecular weight in the range of from about 1,500 to about 6,000, and said cured coating has a thickness of from 2.5 to 6 mils.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04240

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC4:** C08F 226/02, 283/04, 283/06; C08G 18/10, 18/67; G02B 6/02, 6/16; **US CL:** 522/96, 95; 525/455; 526/301; 528/75

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
US	522/96, 95; 525/455; 526/301 528/75

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 4,269,680 (ROWE) 26 MAY 1981. SEE COLUMNS 3-8, COLUMN 15, PARAGRAPH 1, COLUMN 10, LINES 13-17 AND COLUMN 16, LINES 16-31.	1, 7, 8, 12, 13, 15, 17, 18, 20-22
Y	US, A, 4,751,273 (LAPIN ET AL) 14 JUNE 1988. SEE COLUMN 1, PARAGRAPHS 2 AND 3, COLUMN 6, LINES 5-13, COLUMN 7, LINES 53-58, COLUMN 8, LINES 25-29, COLUMN 5, LINES 17-21 AND COLUMN 3, LINES 33-48.	1-11, 15-18 --
Y	"CATIONIC POLYMERIZATION-IODIUM AND SULFONIUM SALT PHOTINITIATORS" J.V. CRIVELLO, FROM "INITIATORS-POLY-REACTIONS- OPTICAL ACTIVITY" SPRINGER-VERLAG: BERLIN HEIDELBERG NEW YORK TOKYO 1984. 62 ADVANCES IN POLYMER SCIENCE; SEE PAGES 13-14 (ESPECIALLY P. 14, PARAGRAPH 3).	1, 3, 15, 16, 18
A	U.S. A, 4,806,574 (KRAJEWSKI ET AL) 22 JULY 1985.	21, 22
A	US, A, 4,798,852 (ZIMMERMAN ET AL) 28 JANUARY 1987	21, 22

\* Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

13 NOVEMBER 1989

Date of Mailing of this International Search Report

09 DEC 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

SUSAN BERMAN



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